# Heat Transfer And Combustion in Multiphase Systems

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## Lecture 16
## Transport processes at interface with key concepts-II

The last class we stopped and said what wetability is, now this one we should also describe that it is some cases as I said there is a relative motion right between the solid and the liquid okay. So, we will try to understand why there is a relative motion and what governs the relative motion essentially.

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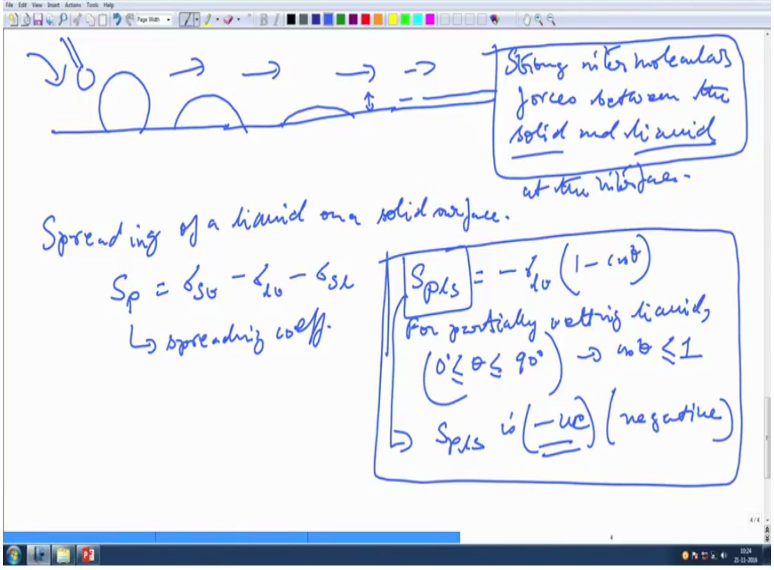

Strong inter molecular forces between the solid and liquid at the interface.

Spreading of a liquid on a solid surface.

$S_p = \sigma_{SV} - \sigma_{LV} - \sigma_{SL}$

↳ spreading coeff.

$\boxed{S_{PLS}} = -\sigma_{LV}(1-\cos\theta)$

For partially wetting liquids

$(0° \le \theta \le 90°) \rightarrow \cos\theta \le 1$

↳ $S_{PLS}$ is $(-ve)$ (negative)

So, we are going to do spreading of our liquid on a solid surface okay. So, if we define something like a spreading coefficient Sp it is basically given by Sigma Sv - Sigma Lv - Sigma Sl okay. So, the spreading coefficient this is called the spreading coefficient. It is a measure of the ability of the liquid to spread over a solid substrate.

If I define it, it is the measure of the ability of the liquid to spread over the solid substrate okay, whatever solid substrate that we are speaking of okay. Now in the same context if it is liquid solid Spls, we can substitute the definition okay of the relationship between the contact angles and this is what we get.

So, it is sigma Lv multiplied by 1 - cos theta, now for partially wetting liquid or partially wetting liquid okay your theta if you recall the definition theta was always like this, right, okay. So, therefore this leads to cos theta is always less than equal to 1. So, therefore this implies that this Spls is always negative, okay.

So, liquid will partially weight and form an equilibrium contact angle right. So, when it is negative when this is negative this will the liquid will spread and it will form a new equilibrium contact angle, got it, okay. So, this is the basic definition of the spreading of a liquid. So, this is the spreading coefficient.

So, you can calculate the spreading coefficient okay and you can determine that whether it is positive or negative. Depending on if it is negative the liquid will spread okay.

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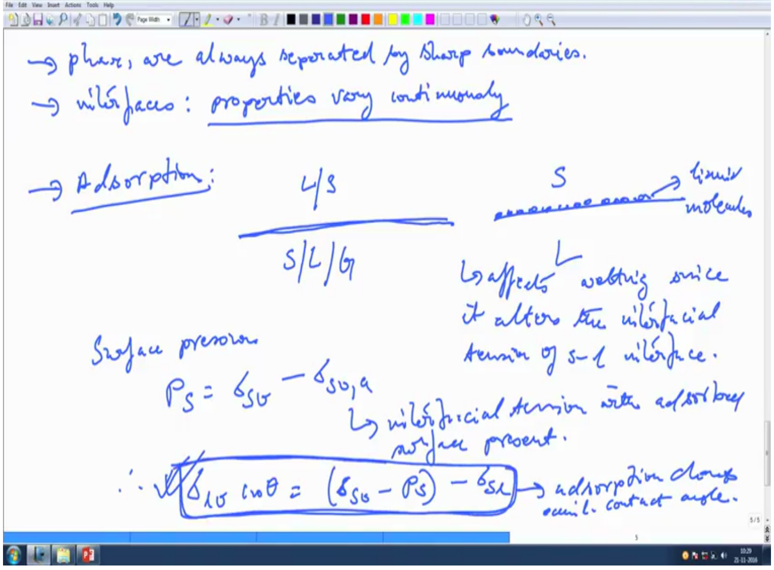

→ phases are always separated by sharp boundaries.

→ interfaces : properties vary continuously

→ Adsorption:

L/S

S/L/G

S

liquid molecules

L

↳ affects wetting since it alters the interfacial tension of s-l interface.

Surface pressure

$$P_S = \sigma_{SV} - \sigma_{SV,a}$$

↳ interfacial tension with adsorbing surface present.

$$\therefore \boxed{\sigma_{LV}\cos\theta = (\sigma_{SV} - P_S) - \sigma_{SL}} \rightarrow$$ adsorption changes equil. contact angle.

Now let us look at another interesting thing, now so, far we have said the phases are you know always separated okay separated okay by sharp boundary, got it. So, they are always separated by sharp boundaries that is one of our assumption okay. But in reality most of the interfaces if you look at it interface are; where the properties vary continuously rather than having a sharp jump, right, okay.

So, rather than having a sharp jump the property is very continuously across the interface okay. So, how some of these things happen we will take up take a look and how that actually affects the corresponding absorption the corresponding wetting behaviour right. Now one important phenomena that happens in this cases is that it is something called adsorption.

And how adsorption plays a role over here, we will see okay. So, say you have a solid and a liquid there is interface okay there is interface, thick or thin okay, you can have a solid liquid gas whatever is the other medium of the other phases okay. Now what happens is that in some of these cases this interface retains the molecules or the other phase okay.

So, if it is a solid it retains some of the liquid okay. So, let us take an example that you have a solid boundary there is a liquid over here. So, the solid interface, solid side of the interface basically retains some of the liquid molecules okay. It basically gets adsorbed on the surface okay. Now as soon as it gets absorbed the liquid molecules it affects the wetting behaviour right.

Because it alters the interfacial tension of the solid and the liquid interface, correct, right. So, the absorption what happens is that this layer that it forms okay where some of the liquid molecules are actually retained okay, on the solid substrate okay, on the solid side of the interface okay. So, this basically affects wetting okay, since it alters the interfacial tension of solid liquid interface okay.

So, the surface pressure if we consider something like a surface pressure, how would you write it this Ps will be nothing but Sigma Sv right minus Something like Sigma Sv adsorbed, okay. It can happen between any two interfaces by the way okay. So, this is the additional surface this is the surface tension with the adsorbed surface present.

The interfacial tension with adsorbed surface present in other words it basically alters the pressure the surface pressure okay. Now if we cast if we take the same relationship and substitute it in our Young's equation okay. What will happen is that Sigma lv and this is an important relationship cos theta is given by Sigma Sv - Ps - Sigma Sl okay.

So, adsorption basically, now if you want to find out the cos theta which is the equilibrium contact angle. So, adsorption changes equilibrium contact angle okay, adsorption changes the equilibrium contact angle okay. So, if you can see this particular relationship over here okay, this actually shows that this is a revised relationship when you actually have this adsorbed layer which is present on the surface okay.

So, based on that it is very easy to determine the revised relationship which shows that the equilibrium contact angle is supposed to change because of this, okay.
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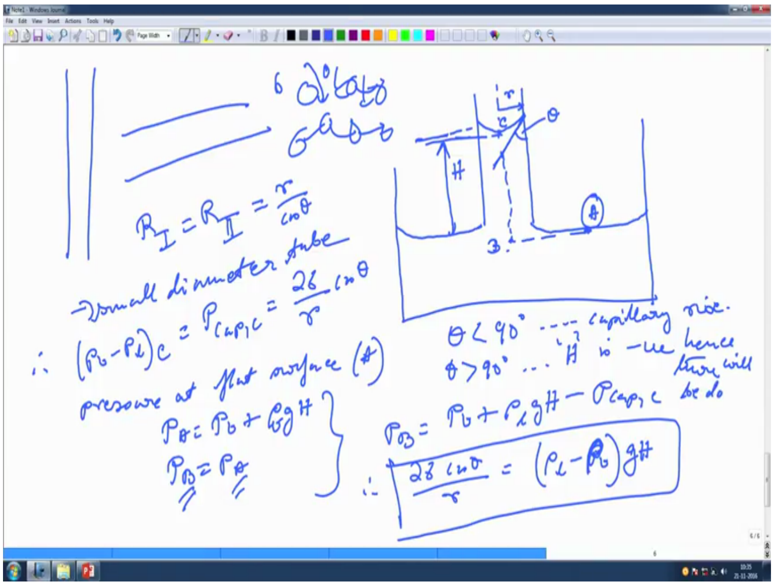

$R_I = R_{II} = \frac{r}{\cos\theta}$

→ small diameter tube

$\therefore (P_v - P_l)_C = P_{cap,C} = \frac{2\sigma}{r}\cos\theta$

pressure at flat surface (A)

$P_A = P_v + \rho_v g H$

$P_B = P_A$

$P_B = P_v + \rho_l g H - P_{cap,C}$

$\therefore \boxed{\frac{2\sigma\cos\theta}{r} = (\rho_l - \rho_v) g H}$

θ < 90° .... capillary rise.

θ > 90° ... 'H' is −ve hence there will be do

Now having done that, now let us look at some of the behaviour of this liquids okay. The surface tensions the theta and the capillary pressure etc how do they determine the behaviour of liquids in like small tubes or channels or porous media. So, if you have a tube like this you know or you can have channels, okay, channels drawn okay.

And it can have porous media basically porous wick's and you can have this kind of a meniscus is to inform okay. So, all these things we can try to look at it in some details over here. So, let us take the figure and how let me draw it properly. So, something like this, okay. This is capillary tube basically maybe a little exaggerated okay at this point.

This is marked as A equivalent point is marked as B over here, okay. Now this radius is basically driven by small r okay and this is the contact angle that it makes this contact angle given by theta okay. And so, this is a Point C on the surf, on the and sorry this is H which is a height of this liquid column okay.

So, here if you recall RI or RI = RII = r cos theta okay. This is a very small tube it is a very narrow tube small diameter tube. And if you look at the tube it has got the following there is a height H okay, there is this points A and B, it makes an angle with the walls which is about theta and that point in the meniscus is given by C okay and so that is the rough configuration that we have.

And of course there is the three-phase forces that are acting on it okay. Now so, therefore Pv -Pl capillary at C basically, so, the capillary pressure at C is basically given by 2 sigma by r cos theta right okay. It is given by 2 sigma by r cos theta, if they divide is 2 sigma by r, r is given by this r by cos theta so you can imagine, what it is.

So, the at the flat surface that is the flat portion of the meniscus, at flat surface A is given by PA = Pv + Rho gH right, the height of the liquid column is a vapour pressure plus that particular pressure. PB must be equal to PA because they are at the same horizontal level right. So, these from these two relationships we can get PB = Pv+ Rho l gH okay.

The previous one was a Rho v okay so Rho lgH - P cap C okay. So, therefore now 2 Sigma cos theta by r = Rho l - Rho v, sorry Rho, Rho is not P into gaH okay. So, you can imagine, so, there is a simple capillary rise within this particular tube okay. What we have done is that the pressure here is nothing but the vapour pressure plus whatever is the liquid column whatever is the vapour column, that is sitting above it okay.

Then the pressure at Pv we must be equal to PA right, because they are the same horizontal levels okay and then it is just a matter of substitution okay. And by substitution and doing the cap introducing the capillary pressure we get this particular expression over here. So, this is the final form okay.

So, if your theta now is less than 90 degrees what can happen the capillary rise can be seen okay. It can be seen, so, we will get a capillary rise right. If theta is greater than 90 degrees okay the capillary rise H, H is negative okay. And hence there is, there will be a depression no raise, there will be depression it would not raise right, okay. So, it cannot be, okay.

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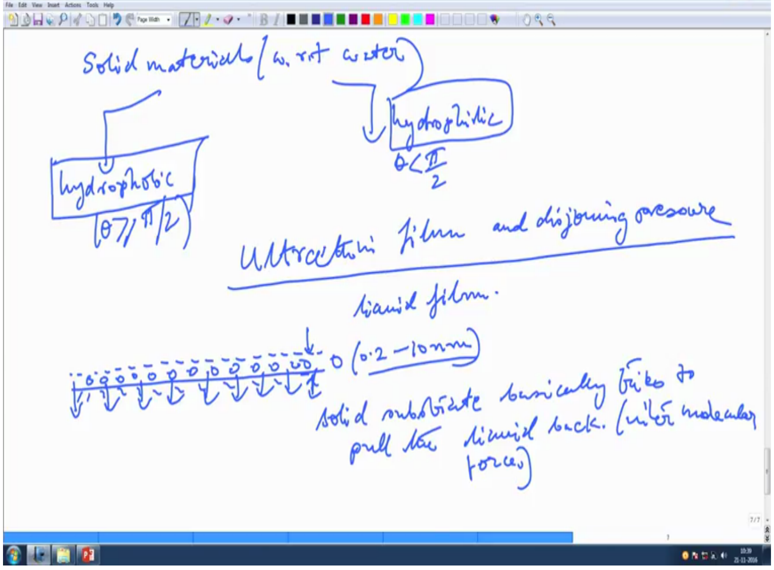

Solid materials (w. r.t water)

hydrophobic

$(\theta \geq \pi/2)$

hydrophilic

$\theta < \frac{\pi}{2}$

Ultrathin film and disjoining pressure

liquid film.

(0.2 - 10nm)

solid substrate basically tries to pull the liquid back. (inter molecular forces)

So, when you actually have solid materials with respect to water say for example we can actually have two classes of substances hydrophobic okay where theta is greater than equal to PI by 2. And you have hydrophilic which we already stated earlier. Now it is a formal definition is less than PI by 2 okay.

Where are hydrophobic substrates are used there are plenty. You can have it for waterproofing that means you are waterproofing for example that you ware or windshield if you want to protect your windshield from the water okay. And it can be also used for removal of water okay.

So, if you want to just water have water roll off. There are clothing's which are also made in that way. It can be also removal of oil from water okay. So, you can use the hydrophobic substances for a variety of things okay. And this is an art these days we can make hydrophobic substrates of different kinds.

Hydrophilic, on the other hand okay, basically in a water-loving kind of a thing, okay. So, it is used as sealants, cleaners, surgical instrument many other things okay. So, there are a lot of usage of the hydrophilic substrate okay. So, we have done what hydrophilic, hydrophobic means and we have done also that how a liquid can actually rise.

And what are thus what are the things that actually govern the movement of the liquid, what is the spreading coefficient and things like that. Now we will introduce a new concept over here which is valid for completely wetted surface that means ultra thin films, okay. And this is called the disjoining pressure.

So, let us look at Ultra Thin Film's and the concept of this disjoining pressure okay, so, when the, when a substrate, let us imagine a substrate like this okay. This is the substrate, there is a very thin layer of liquid which sits on the top of the, substrate is a liquid. So, and the thickness of this liquid film; the order of it is about .2 to 10 nano meter, very good, okay.

It is not a very thick thing; it is a thin film okay. So, in this thin film, the of course the liquid molecules are very close to the solid substrate right. So, there is a very strong pull of the liquid towards solid substrate. So, the solid substrate basically tries to pull the liquid back, okay. So, this is basically due to once again the intermolecular forces okay. Now if capillary pressure if say absent?
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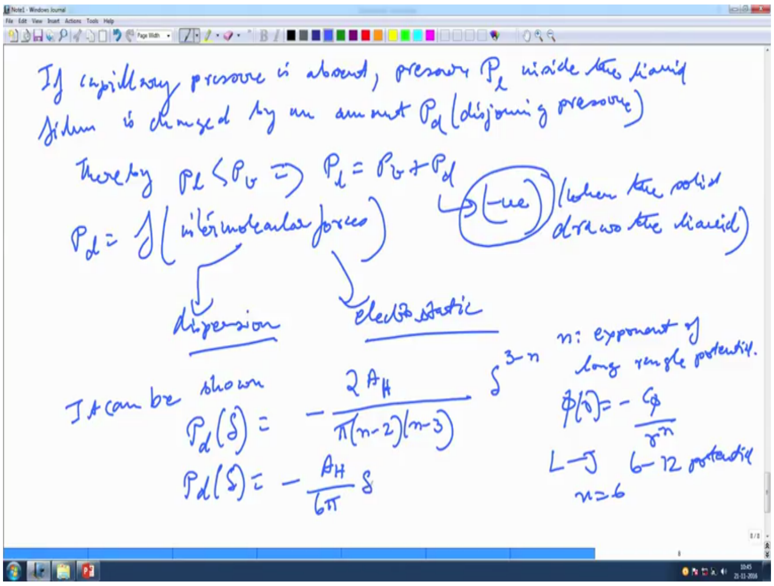

If capillary pressure is absent, pressure $P_l$ inside the liquid film is changed by an amount $P_d$ (disjoining pressure)

Thereby $P_l < P_v \Rightarrow P_l = P_v + P_d \rightarrow (-ve)$ (when the solid draws the liquid)

$P_d = f$(intermolecular forces)

dispersion

electrostatic

It can be shown

$$P_d(\delta) = -\frac{2A_H}{\pi(n-2)(n-3)}\delta^{3-n}$$

$$P_d(\delta) = -\frac{A_H}{6\pi}\delta$$

n: exponent of long range potential.

$$\phi(r) = -\frac{C_\phi}{r^n}$$

L-J 6-12 potential

$n=6$

Let us look at the situation if the capillary pressure is absent okay then the pressure inside the liquid film is changed by a very small amount. Because of this additional pull that is created by the substrate correct. So, if capillary pressure that means because there is no curvature say for example capillary pressure is absent, right.

And then the pressure Pl which is basically the pressure sorry pressure Pl okay, inside the liquid okay liquid film that is it changed by an amount Pd okay. This Pd is called the disjoining pressure okay. So, thereby okay there by the Pl is less than Pv, the vapour pressure, for Pl = Pv + Pd which is the disjoining pressure, okay. So, this disjoining pressure is basically negative when the solid draws the liquid okay.

So, this Pd you can readily see it is a function of the intermolecular forces molecular forces okay which is basically a combination of the dispersion forces and that electrostatic ones because of the combination of these two forces okay. There is a depression okay of the liquid pressure okay and that is done because there is this disjoining pressure which is a negative value.

Which basically makes them solid to pull the liquid towards itself, right, so, let us look at the presentation file.

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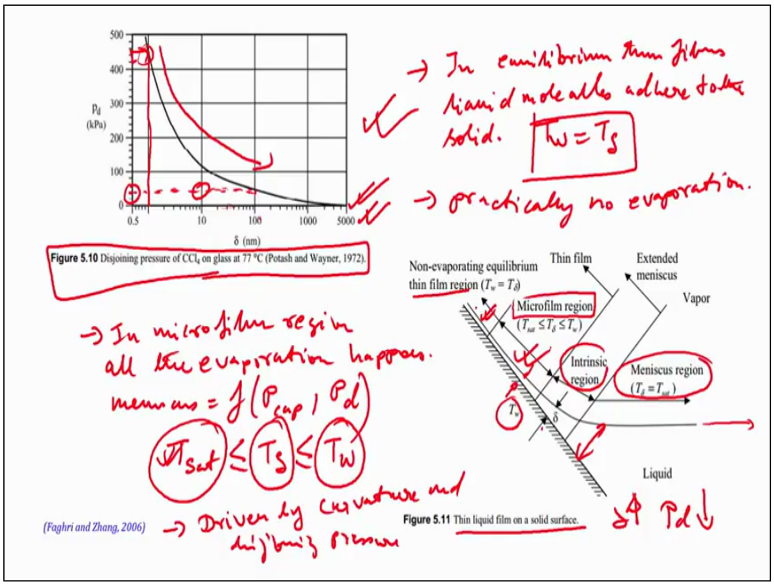

**Figure 5.10** Disjoining pressure of $CCl_4$ on glass at 77 °C (Potash and Wayner, 1972).

**Figure 5.11** Thin liquid film on a solid surface.

(Faghri and Zhang, 2006)

→ In equilibrium thin films liquid molecules adhere to the solid. $\boxed{T_w = T_s}$

→ practically no evaporation.

→ In microfilm region all the evaporation happens.

meniscus = $f(P_{cap}, P_d)$

$T_{sat} \le T_s \le T_w$

→ Driven by curvature and disjoining pressure

δ↑ $P_d$↓

Now, so, let us look at this particular graph over here okay this is basically the disjoining pressure okay and on glass at 77 degrees Celsius okay. And this is of the order of nanometers the horizontal scale that is the thickness of the liquid, liquid layer. So, when it is about 5000 nanometer, which is basically 5 micron. You do not see any disjoining pressure at all right.

It is zero practically non-existent okay. And it shows this exponential type of a decay characteristics right where for example when you are at 100 nanometers the disjoining pressure is actually pretty low right. It is of the order of somewhere around 40 kilopascal's well not low per se but it is actually much lower than when you are going down to a very thin film limit of like .5 nanometer it is very high.

Very high means very, very high like 100 kilopascals is one atmosphere. So, it is four times okay it is basically four times atmosphere okay this is for example is half atmospheric okay in these cases. And it is like 4 times to 5 times atmospheric condition okay. As you move one order so 100 to 10 you get an increase okay and from 10 to 1 basically you get a huge increase in the disjoining pressure okay.

So, this designing pressure is an interesting quantity okay. So, let us look at; so this is one example obviously. Now when we come across to our original thing okay we can show it can be shown and that would require a complete statistical mechanics course. It can be shown that the Pd is a function of this thickness of this layer basically given by 2Ah by irregular Pi n –2, n-3 do not be bothered about these things okay.

N is the exponent of long-range okay potential okay. So, that potential can be something like this okay. So, that is the long-range potential this long-range interaction potential can be represented essentially by the Lenard Jones 6-12 potential okay. We are basically your n becomes equal to 6, so, Ps delta given by 6 Pi delta - 3 okay.

So, this is basically when you use the Lenard-Jones potential, you get that okay. So, Lenard-Jones is a 6-12 potential it is very common in statistical mechanics.

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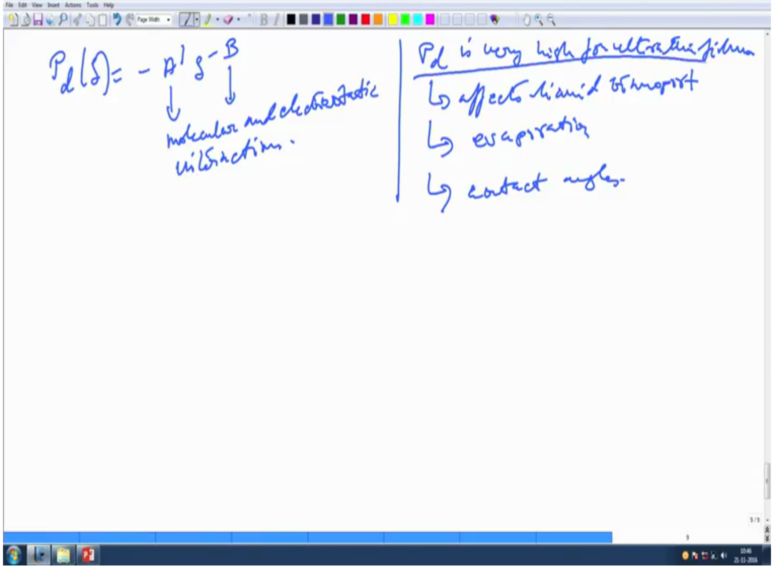

$P_d(\delta) = -A'\delta^{-B}$

molecular and electrostatic interactions.

$P_d$ is very high for ultrathin films

↳ affects liquid transport

↳ evaporation

↳ contact angles.

So, on the other hand most common way of writing this will be –A prime delta - B okay where these depends on the molecular and electrostatic interaction this A prime and B molecular and electrostatic static interaction okay. So, Pd is very high, since Pd, so some of the characteristics is that Pd is very high okay, very high for ultra thin films right that we already got through the example, ultra thin films.

So, it affects your liquid transport okay it affects your evaporation we will see and it affects of course the contact angles okay. So, now, so, this actually shows that Pd is a very important parameter especially when we go down to a very thin film dynamics okay, so, that would be the next and if we look at a situation like this now.

Let us look at the presentation once again and pick the pen. So, let us assume that there is a thin film on a solid substrate. Let us pause this problem first that what this problem essentially entails okay. So, there is a inclined substrate like this inclined or whatever okay. So, this substrate have got a temperature of Tw okay and there is a liquid which is basically wet the surface like this before it goes and forms the principal meniscus over here, right.

So, there is a little this is very similar to the problem that we did when we actually had a wall and there was a thinning of the liquid if you recall. So, it is very much similar to that and it is equivalent okay. Now this region okay, so, it basically this film actually wet’s the surface. If you look at it, it basically wets the surface okay and then it forms the then the curvature increases and it flattens out. So, it is it forms that from that arc like this okay.

Now this can be divided into several parts right okay. So, the liquid spread to the wall to form an extended meniscus that is being interesting part. So, here it is really thin, this region is really thin film region. This region is what we call a microfilm type of region, not that thin but still thin enough. There is an intrinsic region okay and then there is a meniscus region okay.

So, there are three regions non-evaporating thin film, there is a microfilm, there is an intrinsic region, there is a meniscus region okay. So, thin film essentially starts from here and microfilm also you can encompasite within the thin film family essentially, right, okay. So, this is the nature and the scope of this particular problem right.

Now in equilibrium thin film okay the liquid molecules adhere to the surface, so therefore there is practically no evaporation. Now in the non evaporating thin film region okay the temperature of the wall is basically imposed on the liquid right because the liquids are basically liquid molecules are basically adhering to the substrate.

So, in this region okay what we have in the in equilibrium thin film okay, in equilibrium thin films what happens is that the liquid molecules adhere to the solid substrate to the solid, right, okay. As a result of that your Tw becomes equal to T delta okay. So that is the interfacial temperature is equal to the wall temperature okay.

So, there is practically no evaporation okay. Now in the microfilm region, so, in that thin film region nothing happens right. Now it is in a microfilm region where many things start to happen. So, let us remove this so that we can write a few things over here, okay. Now in the microfilm region okay all these operation happens, got it, okay.

The meniscus here in this region is influenced, so the meniscus we can say it is a function of both the capillary pressure as well as the disjoining pressure, right, okay. It is a function of both and you can see that your saturation pressure is less than equal to the T delta which is less than equal to the T wall. So, the interface temperature is not exactly equal to the wall temperature.

Wall temperature is actually a little higher did this is because this is in the slightly thicker region that we are dealing with, right. And this is actually more than a saturation temperature.

This we will show a little later what this exactly means okay. So, the flow in this particular region is driven by curvature if there is a flow curvature and disjoining pressure okay.

Now subsequently as the thickness grows right as delta increases okay the disjoining pressure naturally comes down, right, okay. So, in the microfilm region you actually have a half a flow and evaporation and here both the curvature as well as the disjoining pressure plays a role. Now here we have seen one other thing that there is a change in saturation vapour pressure over a curved interface okay.

Now in thin film both Pd and the capillary effect reduce the saturation pressure compared to the normal condition okay. So, in the thin film region the disjoining pressure this is still the thin-film region right. So, the designing pressures as well as the capillary pressure affect, effectively reduce the saturation pressure compared to the normal condition.

So, in other words there is a change in saturation vapour pressure across a curved interface and in the thin film region the two main players are capillary pressure and the disjoining pressure which basically reduce okay. The saturation pressure compared to any other normal conditions okay.

So, we will in the next class what we are going to do we are going to prove that this is really true and then we will work through the math of interfacial heat and mass transfer including the effect of this disjoining pressure and surface tension and things like that okay before we move on to the phase transfer that mean how the phase transition happens okay.

So, we will stop here in this particular class we will pick up from this particular problem and we will show that why there is a reduction in saturation pressure across the meniscus okay in the thin film region, particularly in the thin film region okay. So, that is it we will see you next class thanks